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(54) Title: PRESSURE AND TEMPERATURE SWING ADSORPTION AND TEMPERATURE SWING ADSORPTION

(57) Abstract

A method is provided for separating one or more volatile contaminant components from a gas using a pressure and temperature swing adsorbent filtration filter bed system containing three or more layers of adsorbent materials characterised in that the layers comprise a first layer of adsorbent material, a second layer of dessicant material and a third layer of material capable of adsorbing contaminants that are not retained by the first layer. Preferably the third layer is capable of adsorbing contaminants of relatively low boiling point, e.g. of boiling teolite.

PRESSURE AND TEMPERATURE SWING ADSORPTION AND TEMPERATURE SWING ADSORPTION.

The present invention relates to methods of treating gases using pressure and temperature swing adsorption, or temperature swing adsorption, together with apparatus and materials for use therein. Particularly the method is directed at purification of gases by removal of particular components therefrom, and the regeneration of adsorbent materials in the apparatus used for the method.

The requirements of an adsorbent system for cyclic filtration processes are not comparable with those of conventional single pass filters. This is because the metallic impregnants on such filters are an undesirable feature as they promote chemisorption. For maximum performance and service life cyclic filtration must therefore proceed reversibly by physical adsorption. Furthermore, the regeneration step must not result in adsorbent degradation; thermal ageing, which can result from overheating of the filter bed, being just one example of such adsorbent degradation. In addition to these considerations, other factors such as particle size and hardness must be assessed when selecting adsorbents for PTSA applications.

Air purification processes, such as those required in collective protection situations wherein air from an external source is purified before delivery to an enclosed area occupied by personnel, typically consists of three stages each requiring a different adsorbent material; (i) removal of high boiling contaminants (eg. boiling point over 50°C), (ii) removal of water vapour, and (iii) removal of low boiling contaminants (eg. boiling point below 50°C). The distinction between high and low boiling contaminants in terms of exact temperature range is not important; the critical requirement is the removal of contaminants having a boiling point between approximately -90°C and 200°C.

The identification of an adsorbent for cyclic filtration of high boiling components is especially demanding as such components are generally strongly physically adsorbed and may be irreversibly retained. Adsorbent characterisation using nitrogen adsorption will elucidate the porous characteristics of an adsorbent but are not useful in prediction of adsorption and regeneration properties; adsorption and desorption data for dimethylmethylphosphonate, ethandiol and a range of other high boiling simulants provides more useful data in this regard.

Using such volatile materials the present inventors have studied a variety of adsorbents and determined that, although many of these have high adsorption capacity, in order for a filter bed to be adequately regenerable only certain types of adsorbent materials meet operational requirements.

Thus in a first aspect of the present invention there is provided a method for separating one or more volatile contaminant components from a gas using a temperature, or pressure and temperature, swing adsorbent filtration filter bed system containing three or more layers of adsorbent materials, characterised in that the layers comprise a first layer of material capable of adsorbing material of relatively high boiling point, a second layer of dessicant material and a third layer of material capable of adsorbing material not adsorbed by the first layer and in that each of the layers may be purged of adsorbed contaminant by a gas having a higher temperature than that from which the contaminants were adsorbed, or having a combination of higher temperature and lower pressure than that from which the contaminants were adsorbed.

The terms first, second and third as applied to these layers relate to the order in which the layers are encountered by gas as during purification. Although these are the only layers illustrated in the following examples, the claims should be construed as including the cases where other layers are present, adjacent to or between the first, second and third layers described herein.

In a preferred embodiment the layers comprise a first layer of mesoporous adsorbent material a second layer of dessicant material and a third layer of material capable of adsorbing contaminants that are not retained by mesoporous material.

Preferably mesoporous layer is an activated carbon and the third layer is preferably capable of adsorbing contaminants of relatively low boiling point, eg. of boiling point less than 50°C; most suitably being a microporous adsorbent. Most preferably the gas from which contaminants are to be removed is an oxygen and/or nitrogen containing gas such as air.

The order of the layers is essential as high boiling point contaminants have been found by the inventors to be retained on all non-mesoporous adsorbents they have tested at high levels, even at temperatures of up to 450°C. Thus by inclusion of a mesoporous adsorbent upstream of the dessicant these downstream layers are protected from the high boiling point contaminants retained on the mesoporous layer.

The efficiency of filtration of high boiling point compounds is not affected significantly by water vapour due to the higher enthalpies of condensation compared with water, whereas the third layer, ideally a molecular sieve such as a zeolite and/or a microporous carbon, and/or mesoporous carbon, will have its efficiency reduced by water vapour. By inclusion of a dessicant layer upstream of the third layer the latter can be protected from water vapour in the gas, which is known to have a deleterious effect on adsorption of many agents by adsorbents such as activated carbons (see C R Hall and R J Holmes (1989) Ads. Sci. and Technol., 6 83; and ISRP Journal, 6, Summer 1992).

The mesoporous layer may be any of the well known mesoporous materials obtainable from suppliers such as Westvaco, Norit, Chemviron, Elf Atochem, UOP, Grace, Dow and Rohm & Haas; typical of those suitable are SA1817, Durferrit, CAR and BAX. The most preferred material of those so far investigated is BAX as it regenerates efficiently and possesses the most appropriate physical properties; ie. relatively large particle size and resistance to oxidation and attrition.

The third layer may employ any of the well known microporous adsorbents such as RB1, NC35, Zeolites (eg 13X) or may be mesoporous carbon. The dessicant layer will preferably be selected from those known to be efficacious in existing pressure swing adsorber drier units, eg. zeolites 13X and 3A.

The arrangement of the layers in the bed should be such that they can each be heated for the purposes of regeneration in the temperature swing adsorption (TSA) or pressure temperature swing adsorption (PTSA) fashion. Such arrangement might conveniently be provided in any fashion that allows controlled heating of the bed layer, and is most conveniently by use of a bed apparatus as described in patent application UK 9422835.0.

The requirements for pure or cleaned air in other applications can also be fulfilled by the present invention. Other applications may require two adsorbent layers or more than three adsorbent layers. The present invention will also result in improvements in adsorbent life and performance in, for example, air drying applications.

In a particular embodiment, the method of the invention is used to provide a collective protection environment for personnel aboard a military or civilian aircraft. Compressed air, heating and cooling means are already available in such an environment.

The method, apparatus and adsorbents of the invention will now be described further by way of illustration only by reference to the following non-limiting examples and figures. Further embodiments falling within the scope of the claims will occur to those skilled in the art in the light of these.

FIGURES

Figure 1 is a graph of amount of nitrogen adsorbed mg g⁻¹ v relative pressure (p/p⁰) to show the mesoporous character for carbons WVA1100 and RB1.

Figure 2 is a graph of thermal desorption of DMMP from BAX and RB1 carbons with changing temperature.

Figure 3 is a histogram showing the adsorption and desorption of DMMP from mesoporous carbons.

Figure 4 is a histogram showing adsorption and desorption of DMMP from microporous adsorbents.

Figure 5 is a graph of water vapour breakthrough measured at 8 bar, 5 dm³ min⁻¹ at 25°C for 13X and 3A molecular sieve adsorbents.

Figure 6 shows adsorption isotherms of HFC134a. on Norbit RB1 at 25°C, 40°C, 55°C, 70°C, 85°C, 100°C, 125°C and 150°C (upper to lower traces).

Figure 7 shows a schematic representation of a filter bed arrangement which might typically be used by the current invention.

Figure 8 shows a schematic representation of a system utilising the current invention to provide a collective protection environment for aircraft personnel.

MATERIALS AND METHODS: Activated carbons, zeolite and polymer based adsorbents were obtained from Westvaco, Norit, Chemviron, Elf Atochem, UOP, Grace, Dow and Rohn & Haas. Nitrogen adsorption for characterising the pore structure was carried out by the method of K S W Sing (1970) 'Surface Area Determination', Edit. Everett and Ottewill, Butterworths, London; pp 25-42. Characterisation of physical properties of the adsorbents also included particle size analysis, packing density and voidage measurements. The ability of the adsorbents to resist attrition during repeated pressure swing cycling was assessed initially using a small packed bed arrangement employing rapid 7 to 0 bar pressure swings (approx. 5000 cycles).

Assessment of adsorption and desorption properties was carried out after first outgassing samples at 120°C, 3mbar. The adsorption of water vapour and high boiling components, including dimethylmethylphosphonate (DMMP, simulant for G agents), and 1,2-ethandiol and 2-chloroethylether (boiling point and structural simulant for H agents) was carried out by exposing samples to each vapour in a dessicator at 30°C

Desorption was measured using thermal gravimetric analysis (TG); a 25 cm³ min⁻¹ airflow was passed through the TG furnace containing the sample during desorption which was then carried out using a 20°C min⁻¹ ramp to 180°C and the sample maintained at that temperature for 75 minutes prior to cooling; in some cases desorption being repeated more than once without re-equilibration, to determine the efficiency of post-challenge regeneration (cycle experiments). 180°C was selected as the regeneration temperature to minimise any risk of adsorbent decomposition or thermal ageing. Adsorption and desorption of low boiling point components including HFC134a was carried out using a semiautomatic microbalance IGA system (Hiden Analytical Ltd UK).

Chemical warfare (CW) agent simulants were selected to reflect both structure and boiling point where possible. Breakthrough data was obtained using a semiautomatic pressure and temperature swing apparatus (Hiden Analytical Ltd, UK).

ADSORBENT FOR FIRST LAYER: HIGH BOILING POINT MATERIAL
ADSORBENT.

Examples of nitrogen isotherms are shown in Figure 1, while Table 1 shows surface area, pore volume data, particle size and oxidation temperature (°C); meso and macro porosity being preferred pore volume characteristics.

Table 1.

Adsorbent	Surface Area m ² g ⁻¹	Pore Vol cm ³ g ⁻¹	Micropore cm ³ g ⁻¹	Mesopore cm ³ g ⁻¹	Particle(mm) length width	Oxidation Temp
RB1	1084	0.485	0.417	0.068	2.3 1.1	380 -400
NC35	1347	0.584	0.528	0.056	5.7 4.0	240 -255
CAR95	1414	0.795	0.489	0.306	3.7 2.4	270 -400
BAX950	1250	0.810	0.392	0.418	4.0 2.0	330 -410
Zeolite 13X	606	0.302	0.225	0.077	2.4 4.8	*
Amberlite		0.875	0.13	0.745	0.4	280 -310

*=temperature stable; RB1 and NC35 are microporous carbons, CAR95 and BAX950 are mesoporous carbons, Zeolite 13X is microporous, XAD4 is a polymer.

Adsorption data for DMMP and the ethandiol are shown in Table 2 and Table 3 with typical desorption profiles being shown in Figure 2. All the materials tested proved to have high adsorption capacity, but predominantly mesoporous materials have significantly greater capacity.

The microporous adsorbents, including 13X zeolite, do not regenerate adequately, retaining more than 30% of the initial adsorbate load; 13X retaining 10% of the adsorbate load at temperatures of above 4500C. This contrasts with the mesoporous adsorbents which retain less than 10%. The behaviour of the different adsorbent types is quite general (see Figures 3 and 4 where loading and residual are the amounts adsorbed and retained respectively as weight percent of DMMP, at the beginning and end of a single desorption experiment).

The effect of pressure swing alone was shown to have little effect on desorption, illustrating the need for a thermal swing.

TABLE 2 Adsorption and desorption of DMMP.

Adsorbent	Amount Adsorbed wt/wt%	180°C Isothermal Region Loss			Residual %
		30min	60min	75min	
RB1	45.6	50.4	61.3	64.5	34.2
NC35	43.8	41.3	51.4	54.8	43.8
CAR95	85.5	75.3	85.3	87.2	12.5
BAX950	91.3	84.6	90.5	91.4	4.3
Zeolite 13X	46.3	65.3	67.8	68.4	34.3
Amberlite XAD4	115.1	97.3	99.4	99.5	0.04

Amount adsorbed is w/w%. Residual loss, determined as % of adsorbent remaining after cooling; original adsorbate loading is 100%.

A comparison of the data in Table 2 with that of Table 3 below, illustrates a strong time dependency of the degree of desorption. indicating that the duration of the heat regeneration phase, including the cooling stage, will be a primary factor in controlling the size and number of beds used. It is notable that a number of the mesoporous materials generated with relatively high efficiency.

Since the TG experiments do not enable airflow through the sample, cycle experiments were carried out to determine the efficiency of post-challenge regeneration. For BAX carbon the residual DMMP loading was ca. 1% (99% desorption after 5 cycles): for Zeolite 13X the residual value was 35% (5 cycles, no further loss detected after the third cycle). These results illustrate that commercially available mesoporous adsorbents exist which possess appropriate adsorption and regeneration characteristics.

TABLE 3 Adsorption and Desorption of Ethandiol.

Adsorbent	Amount Adsorbed wt/wt%	180°C Isothermal Region Loss			Residual %
		30min	60min	75min	
RB1	42.9	59.4	78.4	82.1	16.6
NC35	41.8	65.6	85.5	90.1	8.5
CAR95	86.5	79.2	90.0	90.9	5.4
BAX950	63.7	85.9	94.9	95.2	2.2
Zeolite 13X	27.0	37.6	40.9	41.7	54.9
Amberlite XAD4	45.2	99.4	-0.3	-0.3	-10.8

Negative mass change may represent adsorbent decomposition.

A comparison of BAX with microporous carbon data for nitrogen adsorption indicates that this mesoporous carbon possesses a comparable micropore volume (see Table 1); the difference in regeneration properties possibly reflecting the well developed mesopore structure which probably results in more efficient and rapid transport of the organic chemicals from the micropore structure.

Tables 2 and 3 show that the performance of molecular sieve for water separation purposes in the dessicant layer(s) will be reduced due to fouling if exposed to high boiling compounds; hence illustrating the need for the upstream location of the mesoporous layer. Typical breakthrough measurements for water vapour through dessicant beds are shown in Figure 5 wherein beds were challenged with a saturated airflow.

As low boiling compounds are only poorly adsorbed under humid conditions, penetration of such contaminants through the mesoporous layer, and at least part of the dessicant) bed, will proceed rapidly.

Figure 6 shows characterisation of the microporous adsorbents with adsorption isotherms, showing the regeneration conditions for removal of HFC134a. Similar such measurements using zeolites and mesoporous carbons demonstrate the utility of these materials for separating light gases in the absence of water vapour.

Referring to figure 7, a typical PTSA adsorbent filter bed of the current invention comprises a first layer 1 of mesoporous adsorbent, a second layer 2 of molecular sieve and a third layer 3 of microporous adsorbent. During normal operation, gas to be purified passes through layer 1 first where high boiling chemicals are removed. The gas then passes through layer 2 where water vapour and some chemicals of lower boiling point than those trapped in layer 1 are removed. Finally, the gas passes through layer 3 where chemicals of a low boiling point relative to those trapped by layer 1 are removed.

During regeneration of the filter beds, gas passes through the filter bed in the opposite direction and each of the layers may be heated by one of heaters 4. Each layer has a heater adjacent to it and downstream of it with respect to the direction of gas flow in purge mode.

Referring to figure 8, inlet air I is fed to heat exchanger 1 which provides primary cooling to reduce the air temperature to not greater than 50°C and preferably below 40°C. The inlet air I may be derived from the aircraft auxiliary power unit, engine bleed or from ram air and should be not less than 4 bar, preferably about 7 - 8 bar. Total air demand is regulated by venturi 2. Entrained water and any liquid contamination is removed during passage of the air through coalescer 3. The coalescer should be sited close to the inlet arrangement to the adsorber beds 4a, 4b and the liquid condensate dumped overboard.

The airflow then passes onto adsorber bed 4a, via valve 5a. The product flow, after passing through non-return valve 6 passes into a manifold arrangement. The bulk of the air (perhaps 90%) then passes into the environmental control system supply for the purposes of systems air, and air for the oxygen concentrator (not shown). The remaining air passes through heat exchanger 7 which raises its temperature to about 200°C prior to passage through valve 8b (two way, selectable) and onto adsorber bed 4b. The inlet air temperature to the regenerating bed should be at, or about, 200°C.

The regenerating air, and the contaminants desorbed by it, (all of which flows in the opposite direction to air being filtered) then pass through a further valve 9b as an exhaust flow Z which would preferably be dumped overboard. The flow rate of regenerative air is regulated by a fixed constriction in the inlet pipe downstream of valve 8b. This allows the pressure to fall to about 1 bar during the heating stage.

On completion of the heating stage, bed 4b can be allowed to cool either by natural convection (termination of the regenerative airflow) or by switching the beds and allowing the input air I to flow onto the bed. Preferably a cool air purge E should be applied via valve 8b prior to switching the beds over.

The placement of a flow restrictor downstream of valve 8b also serves to regulate the cooling flow since the manifold feed pressure will be the same for flow rates D and E (this arrangement means that flow rates D and E are the same). On completion of regeneration (and cooling) of bed 4b it becomes the adsorbing bed and 4a becomes the regenerating bed.

Although only two adsorbing beds are shown, the use of more than two are shown, the use of more than two beds is feasible and this may allow the design of a more compact system.

Heat exchanger 7 is shown as two separate units for clarity. In practice, the regenerative airflow would be obtained from a single heat exchanger from an appropriate design of the pipework. The system functions on a fixed cycle time and the valves may be controlled by a cam arrangement or, more preferably, by software.

The filtration system may be sited anywhere within the confines of the airframe to simplify integration, as long as the inlet temperature requirements are met. The system lends itself to incorporation on an aircraft since compressed air and means for heating and cooling are already available.

Use of a filter bed comprising the layered adsorbents as disclosed in the present application allows maximum protection to be achieved using a minimally sized apparatus due to increased capability for efficient regeneration and taking advantage of the temperature and pressure swing facility. This is equally applicable to the temperature swing process, but in this case the beds will need to be larger, owing to the need to remove larger quantities of water vapour which would normally be removed as a result of air compression during the PTSA process.

CLAIMS.

1. A method for separating one or more volatile contaminant components from a gas using a temperature, or pressure and temperature, swing adsorbent filtration filter bed system containing three or more layers of adsorbent materials, characterised in that the layers comprise a first layer of material capable of adsorbing material of relatively high boiling point, a second layer of dessicant material and a third layer of material capable of adsorbing material not adsorbed by the first layer and in that each of the layers may be purged of adsorbed contaminant by a gas having a higher temperature than that from which the contaminants were adsorbed or having a combination of higher temperature and lower pressure than that from which the contaminants were adsorbed.
2. The method of claim 1 where the layers comprise a first layer of mesoporous adsorbent material a second layer of dessicant material and a third layer of material capable of adsorbing contaminants that are not retained by the mesoporous adsorbent.
3. The method of claim 2 where the third layer is capable of adsorbing contaminants of relatively low boiling point.
4. A method as claimed in claim 3 wherein the third layer is capable of adsorbing contaminants of boiling point less than 50°C.
5. A method as claimed in claim 4 wherein the third layer comprises a microporous adsorbent.
6. A method as claimed in claim 5 wherein the third layer comprises zeolite and/or microporous carbon.
7. A method as claimed in claim 5 or 6 wherein the third layer further comprises a mesoporous adsorbent.
8. A method as claimed in any one of preceding claims wherein the second layer is a zeolite.

9. A method as claimed in any one of claims 1 to 8 wherein the gas from which the contaminant components are removed is an oxygen and/or nitrogen containing gas.
10. A method according to claim 9 wherein the gas is air.
11. A method as claimed in any one of the preceding claims wherein the bed layers are individually heated.
12. A pressure and temperature swing adsorber filtration bed comprising three or more layers of adsorbent materials characterised in that the layers comprise a first layer of mesoporous adsorbent material, a second layer of dessicant material and a third layer of material capable of adsorbing contaminants that are not retained by the mesoporous adsorbent.
13. A filtration bed as claimed in claim 12 wherein the third layer is capable of adsorbing contaminants of relatively low boiling point.
14. A filtration bed as claimed in claim 13 wherein the third layer is capable of adsorbing contaminants of boiling point less than 50°C.
15. A filtration bed as claimed in claim 14 wherein the third layer comprises a microporous adsorbent.
16. A filtration bed as claimed in claim 14 wherein the third layer comprises zeolite.
17. A filtration bed as claimed in claim 14 wherein the third layer comprises a mesoporous carbon.
18. A filtration bed as claimed in any one of preceding claims wherein the second layer is a zeolite.

19. A filtration bed as claimed in any one of claims 12 to 18 characterised in that it is a nitrogen and/or oxygen gas purifying filtration bed.
20. A filtration bed as claimed in any one of the preceding claims wherein the bed layers are individually heated.
21. A filtration bed as claimed in any one of claims 12 to 20 and as described in the example.

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Fig.1.

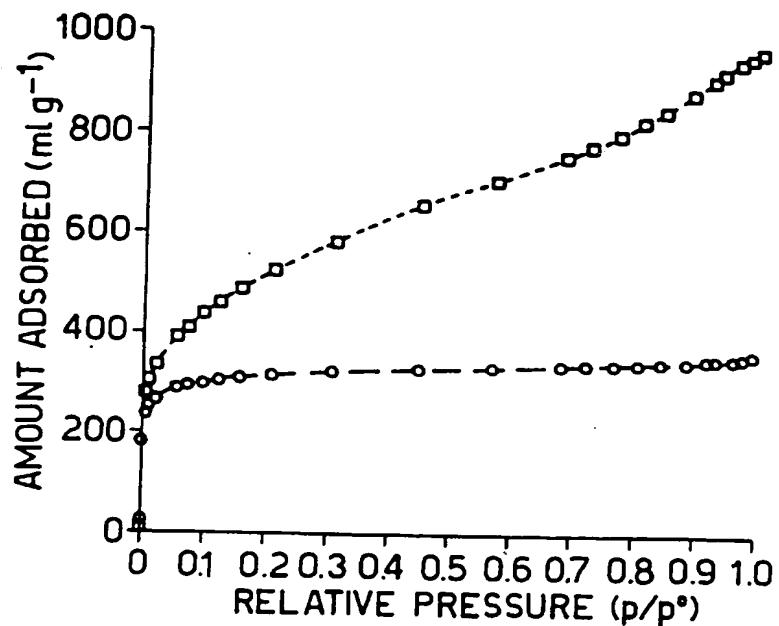
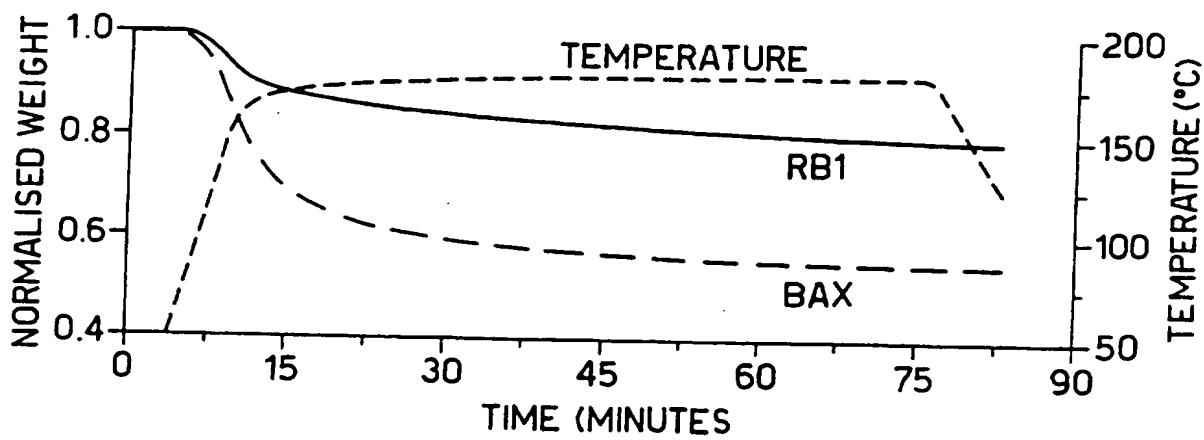


Fig.2.



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Fig.3.

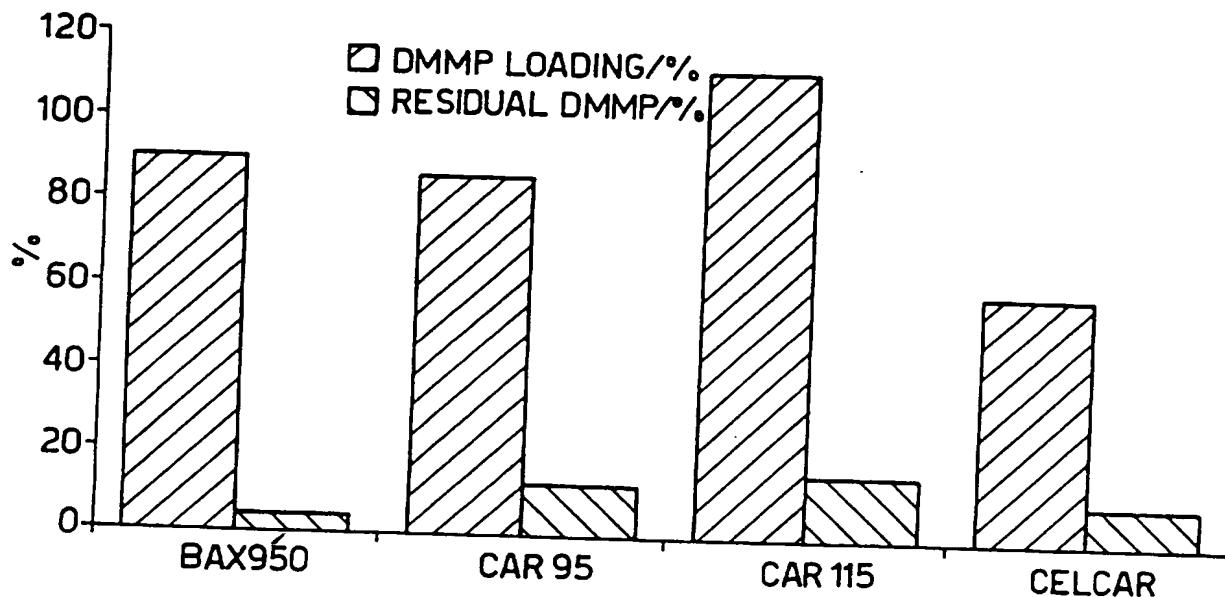
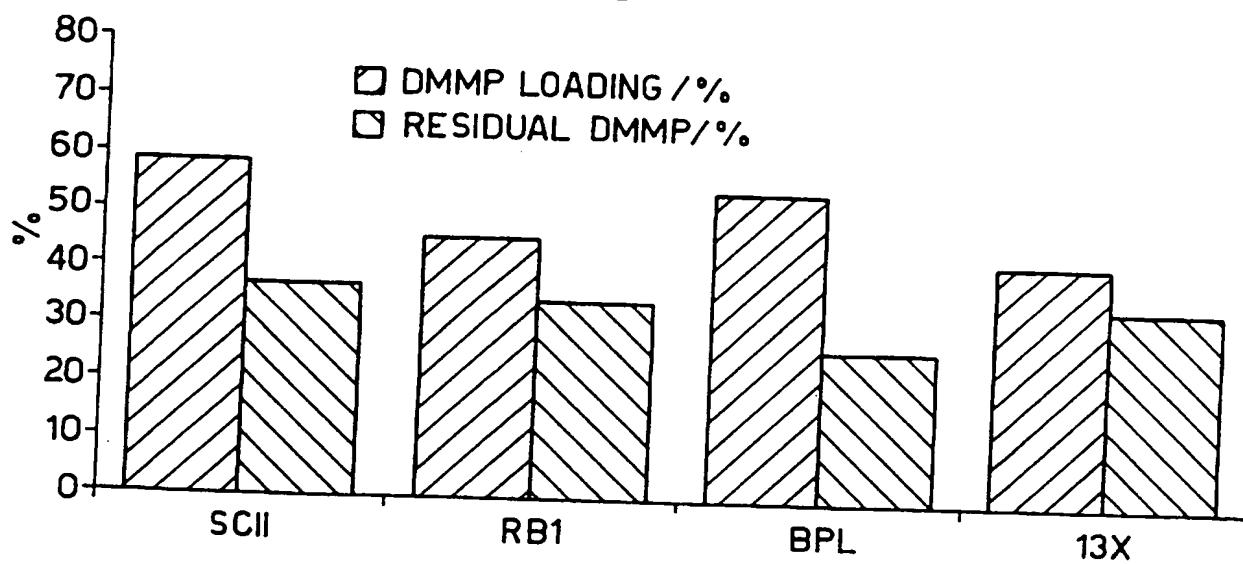


Fig.4.



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Fig.5.

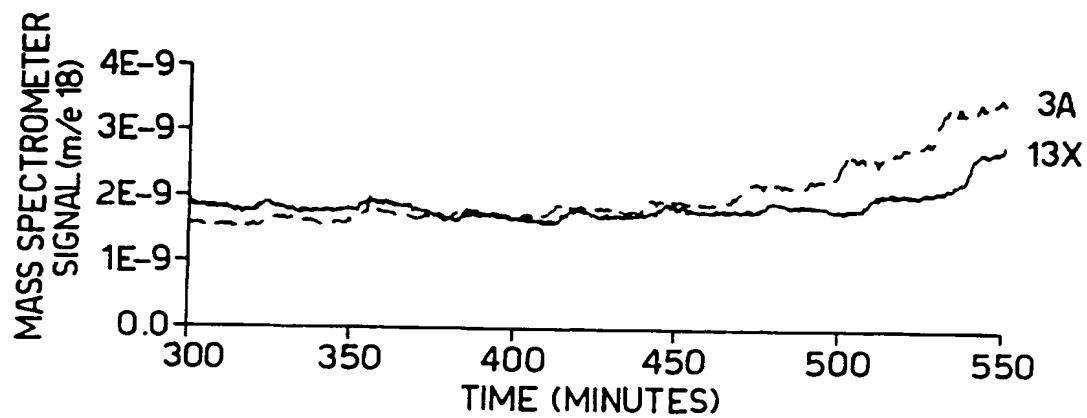
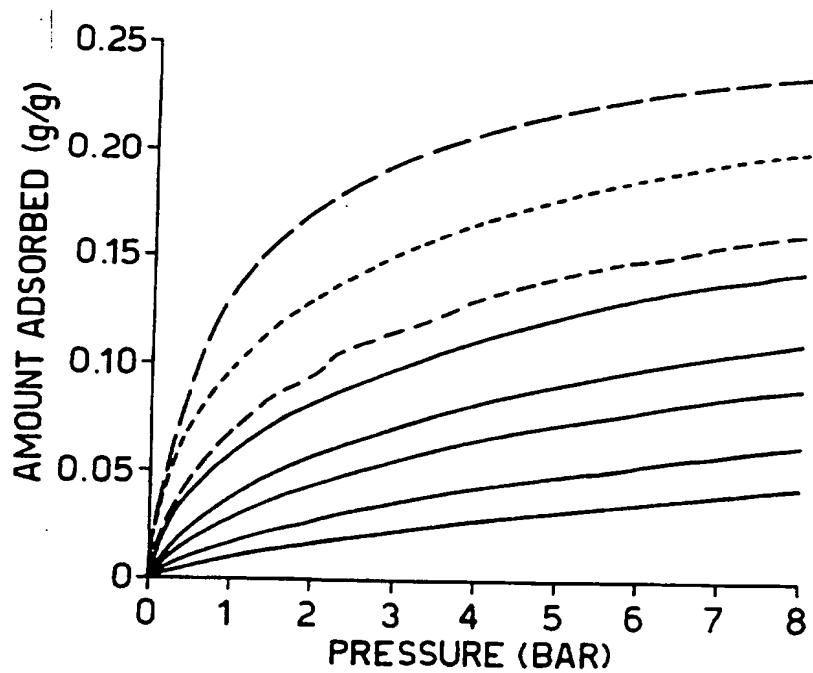


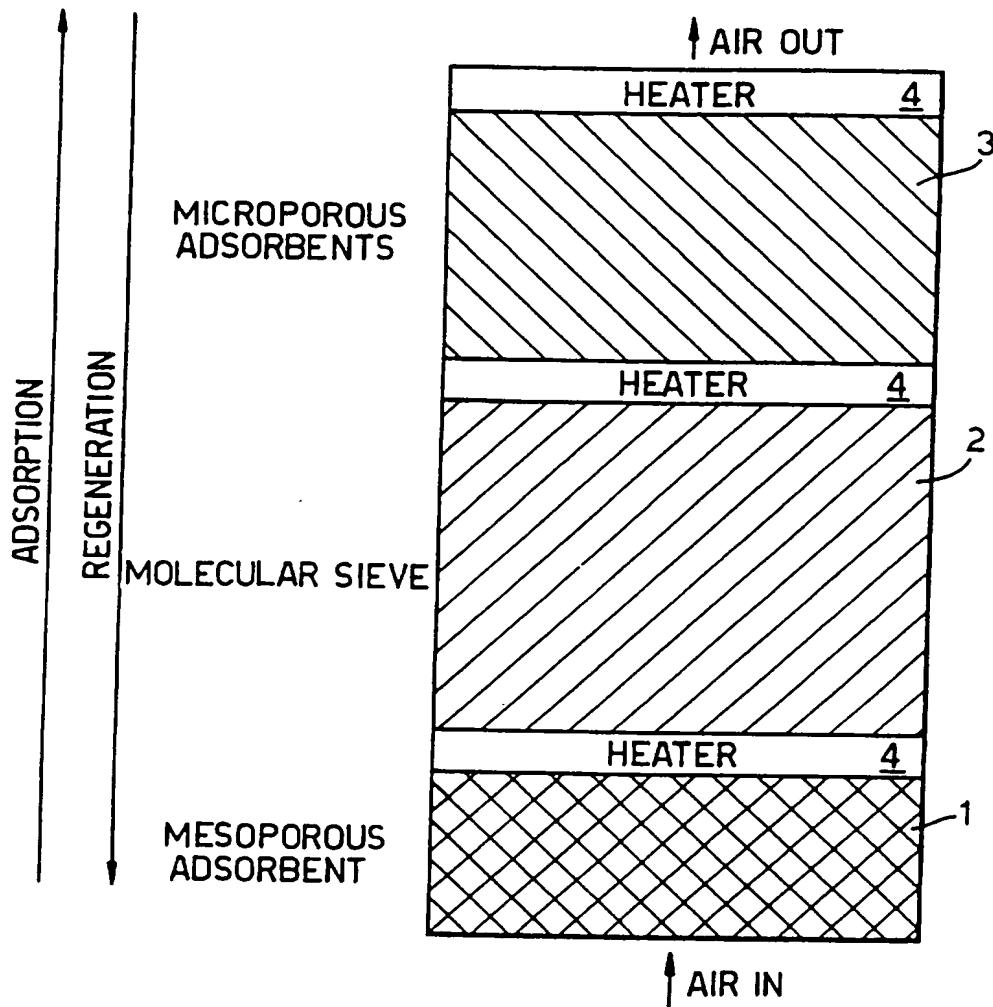
Fig.6.

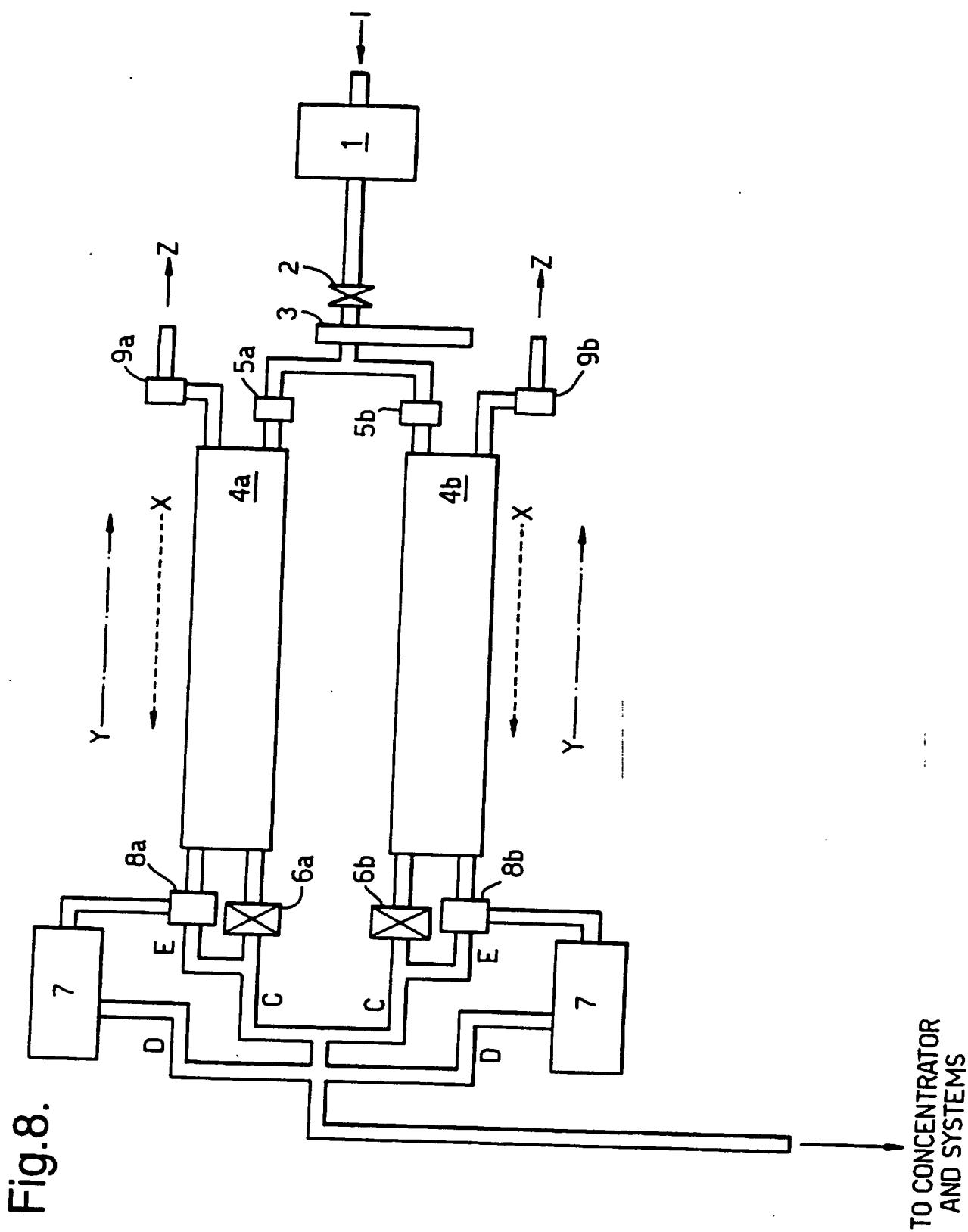


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Fig.7.





INTERNATIONAL SEARCH REPORT

Int'l Application No.

PCT/GB 95/02623

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the file(s) searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 961 919 (CHARLES L. LAMOREAUX) 8	12-14,
A	June 1976 see column 5, line 1 - line 51; figure 1	19,21
A	---	1-4,9,10
A	US,A,2 195 565 (W. J. FRICKE) 2 April 1940	
A	---	
A	US,A,3 844 739 (TURNER ALFREY) 29 October	
1974	-----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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Date of mailing of the international search report

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Bogaerts, M

INTERNATIONAL SEARCH REPORTInternational Application No
PCT/GB 95/02623

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3961919	08-06-76	NONE	
US-A-2195565	02-04-40	NONE	
US-A-3844739	29-10-74	NONE	